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(54) Process for preparation of silyl ketene acetals

Verfahren zur Herstellung von Silylketenacetalen

Procédé de préparation de silyl cétène acétals

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(56) References cited:

EP-A- 0 219 949 EP-A- 0 305 855

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Description

The present invention is a process for the preparation of silyl ketene acetals. The process comprises contacting a mixture comprising an organohydrosilane having a silicon-bonded hydrogen (organohydrosilane) and a vinylic compound with $\text{RhCl}(\text{di-tert-butylsulfide})_2$ as a catalyst at a temperature within a range of 20°C. to 100°C. The $\text{RhCl}(\text{di-tert-butylsulfide})_2$ catalyst demonstrates higher activity than that typically described for rhodium catalysts, allowing for lower concentrations of catalyst and lower reaction temperatures to be used while maintaining high conversion to the desired silyl ketene acetals.

E. Yoshii et al., Chem. Pharm. Bull. 22:2767-2769 (1974), describe the use of tris(triphenylphosphine)chlororhodium as a catalyst for the hydrosilation of several methyl 2-alkenoates with trialkylsilanes. The process was run at 60°C. to 100°C. and a typical catalyst concentration was about 3×10^{-3} mole percent. Typical yields of the process for silyl ketene acetals were reported in the range of 31 percent to 77 percent.

I. Ojima et al., J. Organometallic Chem. 111:43-60 (1976), also describe the use of tris(triphenylphosphine)chlororhodium as a catalyst for the hydrosilation of several methyl 2-alkenoates with trialkylsilanes. The times evaluated varied from one to 12 hours, the temperature from 40°C. to 100°C. and catalyst concentration from about 0.05 to 0.1 mole percent. Yoshii et al. and Ojima et al. observed in addition to their silyl ketene acetals minor quantities of a 1,2-adduct as a by-product.

EP-A-305 855 mentions $\text{RhCl}_3 \cdot (\text{n-Bu}_2\text{S})_3$ as a catalyst for the preparation of silyl ketene acetals.

The present invention is a process for preparation of silyl ketene acetals comprising:

(A) contacting a mixture comprising a organohydrosilane described by formula



and a vinylic compound described by formula



with $\text{RhCl}(\text{di-tert-butylsulfide})_2$ catalyst at a temperature within a range of 20°C. to 100°C.; and
(B) recovering silyl ketene acetals described by formula



where each R is a radical independently selected from a group consisting of alkyls comprising one to 20 carbon atoms, alkoxy comprising one to 20 carbon atoms, cycloalkyls comprising four to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls and aryloxy; each R^1 is independently selected from a group consisting of R and hydrogen; and R^2 selected from a group consisting of alkyls comprising one to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls, triorganosilyl radicals described by formula $-\text{SiR}_3$ where R is as previously described, organooxy radicals described by formula $-(\text{CH}_2)_n\text{OR}^3$ where n is an integer from one to ten and R^3 is selected from a group consisting of alkyls comprising one to 20 carbon atoms, cycloalkyls comprising four to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls and triorganosilyl radicals described by formula $-\text{SiR}_3$ and R is as previously described.

The present process can be run in any standard reactor for contacting a mixture and catalyst. The process can be run as a continuous process or as a batch process. Preferred is a continuous process conducted in a stirred-tank reactor. For best results, it is preferred that the reactor be purged with an inert gas, such as nitrogen gas containing two volume percent oxygen, prior to addition of the reactants.

The reactants can be added to the reactor either as a preformed mixture or individually. When the process is run as a batch process, it is preferred that the vinylic compound, a free radical inhibitor if used, and $\text{RhCl}(\text{di-tert-butylsulfide})_2$ catalyst be added to the reactor to form an initial mixture, then the organohydrosilane be added to this initial mixture at a controlled rate. By "controlled rate", it is meant that the organohydrosilane is added to the reactor at a rate to maintain the temperature of the mixture within the desired range. The rate of addition of the organohydrosilane will depend upon such factors as the size of the reactor, chemical formula of reactants and the use of alternative temperature control means. Organohydrosilanes useful in the present invention are described by formula (1). The organohydrosilane

contains three substituents R, where each R is a radical independently selected from a group consisting of alkyls comprising one to 20 carbon atoms, alkoxy radicals comprising one to 20 carbon atoms, cycloalkyls comprising four to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls and aryloxy radicals. The radical R can be, for example, methyl, ethyl, propyl, iso-butyl, tert-butyl, pentyl, cyclopentyl, cyclohexyl, 3,3,3-trifluoropropyl, perfluoropropyl, chloromethyl, phenyl, tolyl, xylyl, naphthyl and phenoxy. Preferred is when R is an alkyl comprising one to six carbon atoms. Most preferred is when R is methyl.

Vinylic compounds useful in the present process are described by formula (2). The vinylic compound contains substituents R¹, where each R¹ is independently selected from a group consisting of R and hydrogen and R is as previously described.

The vinylic compound contains substituent R², where R² is selected from a group consisting of alkyls comprising one to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls, triorganosilyl radicals described by formula -SiR₃ where R is as previously described and organooxy radicals described by formula (CH₂)_nOR³ where n is an integer from one to ten and R³ is selected from a group consisting of alkyls comprising one to 20 carbon atoms, cycloalkyls comprising four to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls and triorganosilyls of formula -SiR₃ and R is as previously described. R² can be, for example, methyl, ethyl, phenyl, trimethylsilyl, trimethoxysilyl, dimethylphenylsilyl and trimethylsilylethoxy. Preferred is when R² is selected from a group consisting of methyl, trimethylsilyl and trimethylsilylethoxy.

The organohydrosilane is added to the process at a concentration of about stoichiometric equivalence to about 20 mole percent excess in relation to the vinylic compound. Preferred is when the organohydrosilane is added to the process at a concentration of about one to five mole percent excess.

The present process can employ a free radical inhibitor that is effective in preventing polymerization of the vinylic compound used in the process. In a preferred process, the free radical inhibitor is combined with the vinylic compound prior to forming a mixture of the vinylic compound with the organohydrosilane. The free radical inhibitor can be, for example, 2,6-di-tert-butyl-4-methylphenol (BHT), hydroquinone and hydroquinone monomethyl ether.

The concentration of free radical inhibitor added to the process is that effective in reducing or preventing polymerization of the vinylic compound and will be dependent upon the particular free radical inhibitor employed. When the free radical inhibitor is BHT, a useful concentration of the free radical inhibitor is within a range of 0.001 to 0.002 mol of BHT per mole of vinylic compound.

The catalyst employed in the present process is RhCl(di-tert-butylsulfide)₂, i.e. RhCl[(CH₃)₃C₂S]₂. The RhCl(di-tert-butylsulfide)₂ catalyst is added to the process at a concentration within a range of 20 ppm to 300 ppm, based on the concentration of rhodium. A preferred concentration of the catalyst is within a range of 50 to 200 ppm, based on the concentration of rhodium. The RhCl(di-tert-butylsulfide)₂ catalyst can be prepared by standard procedures for reacting RCl₃ and di-tert-butylsulfide.

The present process can be conducted at a temperature within a range of 20°C. to 100°C. Preferred is a temperature within a range of 40°C. to 70°C.

The mixture comprising the organohydrosilane and vinylic compound is contacted with the RhCl(di-tert-butylsulfide)₂ catalyst for a time period of 0.1 hour to ten hours. Preferred is a contact time of 0.5 hour to five hours. Most preferred is a contact time of 0.75 hour to two hours.

Silyl ketene acetals (SKAs) as described by formula (3) are recovered from the present process. Recovery of the SKAs can comprise storing or using the SKAs without further treatment or can comprise further processing, for example, distillation, to separate the SKAs from unreacted feed materials and by-products.

The following examples are offered to illustrate the present invention. These examples are not intended to limit the claims provided herein.

45 Example 1

The specificity of RhCl(di-tert-butylsulfide)₂ to catalyze the reaction of trimethylsilane with methylmethacrylate to form trimethylsilyldimethyl-ketene acetal was evaluated. The reactor consisted of a 500-mL flask equipped with a dry-ice condenser, a magnetic stirrer and a thermometer. The reactor was charged with 111 g of methylmethacrylate (MMA), 50 1.23 g of a toluene solution containing 0.0285 g of RhCl(di-tert-butylsulfide)₂ catalyst and 0.297 g of 2,6-di-tert-butyl-4-methylphenol (BHT). This mixture was stirred and heated to 55°C. under a constant purge with a 2% oxygen and 98% nitrogen mixture. After the mixture reached 55°C., heat was removed and 107 g trimethylsilane (Me₃SiH) was fed to the reactor as a gas. The cumulative stoichiometric amount of trimethylsilane added at the end of each sampling period is provided in Table 1 in the column labelled "%Me₃SiH." The trimethylsilane feed rate was regulated to maintain the temperature within the reactor at 55°C. to 60°C. Samples were taken during the course of the trimethylsilane addition to analyze for product formation. These samples are identified in Table 1 as samples 1 through 5 and the corresponding time for collecting the sample after the initiation of addition of trimethylsilane is given in the column labelled "Time." Each sample was analyzed using gas chromatography with a mass spectrometer detector (GC/MS).

The results are presented in Table 1 as the area percent under the GC/MS trace for each of the following: MMA, trimethylsilyldimethyl-ketene acetal, i.e., $(\text{CH}_3)_2\text{C}=\text{C}(\text{OMe})(\text{OSiMe}_3)$, labelled SKA1; $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}(\text{OMe})(\text{OSiMe}_3)$, labelled CA1 and $\text{Me}_3\text{SiCH}_2\text{C}(\text{CH}_3)\text{HCOOMe}$, labelled VA1.

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TABLE 1

| RhCl(di-tert-butylsulfide) ₂ Catalyzed Reaction of Trimethylsilane With Methylmethacrylate | | | | | | |
|---|---------|----------------------|--------------------|------|------|-----|
| Sample No. | Time(h) | %Me ₃ SiH | GC/MS Area Percent | | | |
| | | | MMA | SKA1 | CA1 | VA1 |
| 1 | 0.3 | 10 | 71.0 | 16.0 | 2.8 | 0.2 |
| 2 | 1.2 | 36 | 32.5 | 38.4 | 6.4 | 0.3 |
| 3 | 2.2 | 72 | 7.9 | 71.0 | 10.0 | 0.4 |
| 4 | 3.0 | 92 | 1.4 | 75.0 | 6.9 | 0.6 |
| 5 | 3.5 | 110 | 0.1 | 80.5 | 4.6 | 0.7 |

Example 2

A comparison of the specificity of RhCl(di-tert-butylsulfide)₂ and RhCl₃.3H₂O to catalyze the reaction of trimethylsilane with trimethylsilylhydroxyethylmethacrylate (TMS-HEMA) to form O-trimethylsilyl-O-trimethylsilyl-hydroxyethylmethacrylate (SKA2) was evaluated.

In a first run, 290 g of TMS-HEMA, 1.34 g of toluene solution containing 0.039 g of RhCl(di-tert-butylsulfide)₂ and 0.16 g of BHT were added to the same reactor as described in Example 1. This mixture was stirred and heated to 55°C. under a constant purge with a 2% oxygen and 98% nitrogen mixture. After the mixture reached 55°C., heat was removed and 117 g of trimethylsilane was fed to the reactor as a gas. The trimethylsilane feed rate was regulated to maintain the temperature within the reactor a 55°C. to 60°C. The cumulative stoichiometric amount of trimethylsilane added at the end of each sampling period is provided in Table 2 in the column labelled "%Me₃SiH." Samples were taken at various times during addition of the trimethylsilane and analyzed by GC/MS, as described in Example 1. The results are presented in Table 2a as the area percent under the GC/MS trace for each of the following: TMS-HEMA, i.e., $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_2\text{OSi}(\text{CH}_3)_3$; $(\text{CH}_3)_2\text{C}=\text{C}\{\text{OSi}(\text{CH}_3)_3\}\{\text{O}(\text{CH}_2)_2\text{OSi}(\text{CH}_3)_3\}$, labelled SKA 2; $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CH}\{\text{OSi}(\text{CH}_3)_3\}\{\text{O}(\text{CH}_2)_2\text{OSi}(\text{CH}_3)_3\}$, labelled CA2; and $(\text{CH}_3)_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{COO}(\text{CH}_2)_2\text{OSi}(\text{CH}_3)_3$, labelled VA2.

Table 2a

| RhCl(di-tert-butylsulfide) ₂ Catalyzed Reaction of Trimethylsilane With TMS-HEMA | | | | | | |
|---|---------|----------------------|--------------------|------|-----|-----|
| Sample No. | Time(h) | %Me ₃ SiH | GC/MS Area Percent | | | |
| | | | TMS-HEMA | SKA2 | CA2 | VA2 |
| 1 | 0.4 | 20 | 75.5 | 19.4 | 1.7 | 0.0 |
| 2 | 0.75 | 40 | 53.1 | 39.2 | 3.5 | 0.0 |
| 3 | 1.0 | 60 | 36.1 | 52.3 | 5.0 | 0.1 |
| 4 | 1.3 | 80 | 19.5 | 73.7 | 6.9 | 0.1 |
| 5 | 1.75 | 110 | 4.1 | 79.5 | 7.8 | 0.1 |
| 6 | 3.0 | 110 | 0.4 | 84.3 | 7.5 | 0.2 |
| 7 | 6.0 | 110 | 0.2 | 85.4 | 7.9 | 0.1 |

A comparison run, using 0.0188 g of RhCl₃.3H₂O dissolved in 0.127 g of methanol as catalyst, was conducted in the same manner as described for the first run. The results are provided in Table 2b. The headings of Table 2b are as described for Table 2a.

Table 2b

| RhCl ₃ .3H ₂ O Catalyzed Reaction of Trimethylsilane With TMS-HEMA | | | | | | |
|--|---------|----------------------|--------------------|------|-----|-----|
| Sample No. | Time(h) | %Me ₃ SiH | GC/MS Area Percent | | | |
| | | | TMS-HEMA | SKA2 | CA2 | VA2 |
| 1 | 2.2 | 50 | 54.9 | 35.2 | 3.4 | 0.1 |

Table 2b (continued)

| RhCl ₃ .3H ₂ O Catalyzed Reaction of Trimethylsilane With TMS-HEMA | | | | | | |
|--|---------|----------------------|--------------------|------|-----|-----|
| Sample No. | Time(h) | %Me ₃ SiH | GC/MS Area Percent | | | |
| | | | TMS-HEMA | SKA2 | CA2 | VA2 |
| 2 | 3.2 | 80 | 18.0 | 64.4 | 6.0 | 1.2 |
| 3 | 4.0 | 91 | 9.8 | 63.5 | 5.9 | 1.9 |
| 4 | 8.0 | 110 | 9.0 | 67.4 | 6.7 | 2.5 |

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The results of this comparison demonstrate that RhCl(di-tert-butylsulfide)₂ causes the desired SKA2 to be formed at a faster rate and results in a higher SKA2 to VA2 ratio, when compared to the RhCl₃.3H₂O catalyzed process.

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The effect of the concentration of RhCl(di-tert-butylsulfide)₂ on the reaction of trimethylsilane with trimethylsilylmethacrylic acid (TMS-MA) was evaluated in a series of runs. All runs in this series used the following general procedure. To the reactor described in Example 1 was added 98.6 g of TMS-MA, RhCl(di-tert-butylsulfide)₂ at a concentration as described in Table 3 and 0.284 g of BHT. This mixture was stirred and heated to 60°C. under a constant purge with a 2% oxygen and 98% nitrogen mixture. After the mixture reached 60°C., heat was removed and 50.8 g of trimethylsilane was fed to the reactor as a gas. The trimethylsilane feed rate was regulated to maintain the temperature within the reactor at 55°C. to 60°C. A sample for analysis was taken at the times indicated in Table 3, for each concentration of RhCl(di-tert-butylsulfide)₂ tested. The concentrations are presented in Table 3 as parts per million rhodium. Each sample was analyzed by GC/MS and the results are reported in Table 3 as area percent under the GC/MS trace for each of the following: TMS-MA, i.e., CH₂=C(CH₃)COOSi(CH₃)₃; (CH₃)₂C=C{OSi(CH₃)₃}₂, labelled SKA3; H₂C=C(CH₃)CH{OSi(CH₃)₃}₂, labelled CA3; and (CH₃)₃SiCH₂CH(CH₃)COOSi(CH₃)₃, labelled VA3.

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Table 3

| Effect of RhCl(di-tert-butylsulfide) ₂ Concentration on Reaction of Trimethylsilane With TMS-MA | | | | | | |
|--|---------|--------|--------------------|------|-----|-----|
| Run No. | Time(h) | PPM Rh | GC/MS Area Percent | | | |
| | | | TMS-MA | SKA3 | CA3 | VA3 |
| 1 | 4.0 | 50 | 40.8 | 44.1 | 2.1 | 0.7 |
| 2 | 4.0 | 100 | 1.2 | 80.6 | 3.9 | 0.6 |
| 3 | 3.5 | 150 | 3.9 | 78.1 | 3.7 | 0.1 |
| 4 | 4.0 | 200 | 2.1 | 79.5 | 4.6 | 0.3 |
| 5 | 3.0 | 250 | 10.8 | 79.4 | 3.9 | 0.1 |

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Claims

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1. A process for preparation of silyl ketene acetals, the process comprising:

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(A) contacting a mixture comprising a organohydrosilane described by formula



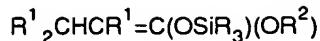
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and a vinylic compound described by formula



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with RhCl(di-tert-butylsulfide)₂ catalyst at a temperature within a range of 20°C. to 100°C.; and
(B) recovering a silyl ketene acetal described by formula



5 where each R is a radical independently selected from a group consisting of alkyls comprising one to 20 carbon atoms, alkoxy radicals comprising one to 20 carbon atoms, cycloalkyls comprising four to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls and aryloxy radicals; each R¹ is independently selected from a group consisting of R and hydrogen; and R² is selected from a group consisting of alkyls comprising one to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls, triorganosilyl radicals described by formula -SiR₃ where R is as previously described and organooxy radicals of formula -(CH₂)_nOR³ where n is an integer from one to ten and R³ is selected from a group consisting of alkyls comprising one to 20 carbon atoms, cycloalkyls comprising four to 20 carbon atoms, halogenated hydrocarbons comprising one to 20 carbon atoms, aryls and triorganosilyls described by formula -SiR₃ and R is as previously described.

10 2. A process according to claim 1 further comprising the addition of a free radical inhibitor.

15 3. A process according to claim 2 where the free radical inhibitor is combined with the vinylic compound prior to forming the mixture of the vinylic compound with the organohydrosilane.

20 4. A process according to claim 3 where the free radical inhibitor is selected from a group consisting of 2,6-di-tert-butyl-4-methylphenol, hydroquinone and hydroquinone monomethyl ether.

25 5. A process according to claim 1 where the concentration of RhCl(di-tert-butylsulfide)₂ is within a range of 50 to 200 ppm.

30 6. A process according to claim 1 where R is an alkyl comprising one to six carbon atoms; R² is selected from a group consisting of methyl, trimethylsilyl and trimethylsilylethoxy; the organohydrosilane is added to the process at a concentration of one to five mole percent excess in relation to the vinylic compound; the temperature is within a range of 40°C. to 70°C.; and contact of the mixture with the RhCl(di-tert-butylsulfide)₂ catalyst is for a time of 0.75 hour to two hours.

Patentansprüche

35 1. Verfahren zur Herstellung von Silylketenacetalen, bei dem man:

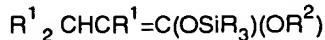
(A) eine Mischung, die ein Organohydrosilan mit der Formel



40 und eine vinyliche Verbindung der Formel



45 enthält, bei einer Temperatur in einem Bereich von 20°C bis 100°C mit RhCl(di-tert.-butylsulfid)₂ als Katalysator in Berührung bringt; und
 (B) ein Silylketenacetal der Formel



50 gewinnt, wobei R jeweils einen Rest bedeutet, der unabhängig aus einer Gruppe ausgewählt ist, die aus Alkylresten mit 1 bis 20 Kohlenstoffatomen, Alkoxyresten mit 1 bis 20 Kohlenstoffatomen, Cycloalkylresten mit 4 bis 20 Kohlenstoffatomen, halogenierten Kohlenwasserstoffresten mit 1 bis 20 Kohlenstoffatomen, Arylresten und Aryloxyresten besteht; R¹ jeweils unabhängig ausgewählt ist aus einer Gruppe, die aus R und Wasserstoff besteht; und R² aus einer Gruppe ausgewählt ist, die aus Alkylresten mit 1 bis 20 Kohlenstoff-

5 atomen, halogenierten Kohlenwasserstoffresten mit 1 bis 20 Kohlenstoffatomen, Arylresten, Triorganosilylresten der Formel -SiR_3 , wobei R wie zuvor beschrieben ist, und Organoxyresten der Formel $\text{-(CH}_2\text{)}_n\text{OR}^3$ besteht, wobei n eine ganze Zahl von 1 bis 10 bedeutet und R^3 aus einer Gruppe ausgewählt ist, die aus Alkylresten mit 1 bis 20 Kohlenstoffatomen, Cycloalkylresten mit 4 bis 20 Kohlenstoffatomen, halogenierten Kohlenwasserstoffresten mit 1 bis 20 Kohlenstoffatomen, Arylresten und Triorganosilylresten der Formel -SiR_3 besteht und R wie zuvor beschrieben ist.

10 2. Verfahren nach Anspruch 1, wobei weiterhin ein Inhibitor für freie Radikale zugesetzt wird.

15 3. Verfahren nach Anspruch 2, wobei der Inhibitor für freie Radikale mit der vinylischen Verbindung vereinigt wird, bevor die Mischung der vinylischen Verbindung mit dem Organohydrosilan hergestellt wird.

20 4. Verfahren nach Anspruch 3, wobei der Inhibitor für freie Radikale ausgewählt ist aus einer Gruppe, die aus 2,6-Di-tert.-butyl-4-methylphenol, Hydrochinon und Hydrochinonmonomethylether besteht.

25 5. Verfahren nach Anspruch 1, wobei die Konzentration von $\text{RhCl}(\text{di-tert.-butylsulfid})_2$ in einem Bereich von 50 bis 200 ppm liegt.

6. Verfahren nach Anspruch 1, wobei R einen Alkylrest mit 1 bis 6 Kohlenstoffatomen bedeutet; R^2 ausgewählt ist aus einer Gruppe, die aus Methyl-, Trimethylsilyl- und Trimethylsilylethoxyresten besteht; das Organohydrosilan in einer Konzentration von 1 bis 5 Molprozent Überschuß in bezug auf die vinylische Verbindung in das Verfahren eingeführt wird; die Temperatur in einem Bereich von 40 bis 70°C liegt; und die Mischung während einer Zeit von 0,75 bis 2 Stunden mit dem $\text{RhCl}(\text{di-tert.-butylsulfid})_2$ als Katalysator in Berührung gebracht wird.

Revendications

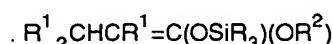
1. Procédé de préparation d'acétals de cétène silylés, procédé comprenant les étapes consistant à :

30 (A) mettre un mélange comprenant un organohydrogénosilane décrit par la formule R_3SiH et un composé vinylique décrit par la formule



35 en contact avec un catalyseur au RhC1 (di-tert-butylsulfure) $_2$ à une température comprise dans une plage de 20° C à 100° C, et

(B) récupérer un acétal de cétène silylé décrit par la formule



40 où chaque R est un radical indépendamment choisi dans le groupe constitué des groupes alkyles comprenant un à 20 atomes de carbone, des groupes alcoxyles comprenant un à 20 atomes de carbone, des groupes cycloalkyles comprenant quatre à 20 atomes de carbone, des groupes hydrocarbonés halogénés comprenant un à 20 atomes de carbone, des groupes aryles et des groupes aryloxyles ; chaque R^1 est indépendamment choisi dans le groupe constitué de R et d'un atome d'hydrogène ; et R^2 est choisi dans le groupe constitué des groupes alkyles comprenant un à 20 atomes de carbone, des groupes hydrocarbonés halogénés comprenant un à 20 atomes de carbone, des groupes aryles, des radicaux triorganosilyles décrits par la formule -SiR_3 où R est tel que précédemment décrit, et des radicaux organoxy de formule $\text{-(CH}_2\text{)}_n\text{OR}^3$ où n est un nombre entier de un à dix et R^3 est choisi dans le groupe constitué des groupes alkyles comprenant un à 20 atomes de carbone, des groupes cycloalkyles comprenant quatre à 20 atomes de carbone, des groupes hydrocarbonés halogénés comprenant un à 20 atomes de carbone, des groupes aryles et des radicaux triorganosilyles décrits par la formule -SiR_3 et R est tel que précédemment décrit.

45 55 2. Procédé selon la revendication 1, comprenant, en outre, l'addition d'un inhibiteur de radicaux libres.

3. Procédé selon la revendication 2, dans lequel on combine l'inhibiteur de radicaux libres avec le composé vinylique

avant de former le mélange du composé vinylique avec l'organohydrogénosilane.

4. Procédé selon la revendication 3, dans lequel l'inhibiteur de radicaux libres est choisi dans le groupe constitué du 2,6-di-tert-butyl-4-méthylphénol, de l'hydroquinone et de l'éther monométhylque d'hydroquinone.
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5. Procédé selon la revendication 1, dans lequel la concentration en RhCl (di-tert-butylsulfure)₂ est comprise dans l'intervalle de 50 à 200 ppm.
6. Procédé selon la revendication 1, dans lequel R est un groupe alkyle comprenant un à six atomes de carbone ; R² est choisi dans le groupe constitué des groupes méthyle, triméthylsilyle et triméthylsilylthoxyle ; on ajoute l'organohydrogénosilane au procédé à une concentration d'une à cinq moles pour cent en excès par rapport au composé vinylique ; la température est comprise dans la plage de 40° C à 70° C ; et on met le mélange en contact avec le catalyseur au RhCl (di-tert-butylsulfure)₂ pendant une durée de 0,75 heure à deux heures.
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